SYMMETRIC CHARGE TRANSFER IN LOW-ENERGY ION-ATOM COLLISIONS

Swati Sinha, et al

Pittsburgh University

Prepared for:

Office of Naval Research

9 February 1975

SPACE RESEARCH COORDINATION CENTER

SYMMETRIC CHARGE TRANSFER IN LOW-ENERGY ION-ATOM COLLISIONS

BY

SWATI SINHA AND J. N. BARDSLEY

SRCC REPORT NO. 218

FEBRUARY 1976

UNIVERSITY OF PITTSBURGH

PITTSBURGH, PENNSYLVANIA

40

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Symmetric Charge Transfer in Low-Energy Ion-Atom Collisions		5. TYPE OF REPORT & PERIOD COVERED Scientific Journal Article 6. PERFORMING ORG. REPORT NUMBER SRCC218
7. AUTHOR(s) Swati Sinha and J. N. Bardsley		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C0098 (ARPA) E(04-3)-1106 (ERDA)
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Pittsburgh Pittsburgh, Pa. 15260		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ARPA Order No. 2686
11. CONTROLLING OFFICE NAME AND ADDRESS Advanced Research Projects Agency 1400 Wilson Boulevard Arlington, Virginia 22209		12. REPORT DATE February 9, 1975 13. NUMBER OF PAGES 40
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Arlington, Virginia 22217		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be submitted to the Physical Review.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Charge transfer; charge exchange, ion-atom collisions; cross section calculations, uranium, calcium, alkali ions, rare-gas ions

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Previous calculations of ion-atom interactions by the pseudopotential and asymptotic methods are used in the computation of the cross section for symmetric charge transfer at energies below 1 keV. The results for Li^+, Na^+, K^+, Rb^+, Cs^+ and Ca^+ ions are compared with data obtained in beam experiments, and by optical pumping techniques. The difference in the cross sections for $^2P_{1/2}$ and $^2P_{3/2}$ ions of Kr^+ and Xe^+ at thermal energies is studied and the predictions are compared with recent mobility measurements. Cross sections are obtained for U^+ -U

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (cont'd.)

collisions, and the dependence of the thermal cross section on the polarizability is described. Symmetric charge transfer of the negative ions H^-, Na^- and Cs^- is discussed briefly.

Symmetric Charge Transfer in Low-Energy Ion-Atom Collisions

Swati Sinha and J. N. Bardsley
Physics Department, University of Pittsburgh, Pittsburgh, Pa. 15260

and

Joint Institute for Laboratory Astrophysics
University of Colorado and National Bureau of Standards
Boulder, Co. 80302

(Submitted to Physical Review)

Sponsored by
Advanced Research Projects Agency
ARPA Order No. 2686

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR under Contract No. N00014-76-C-0098, and by ERDA under Contract No. E(04-3)-1106.

February 1976

Symmetric Charge Transfer in Low-Energy Ion-Atom Collisions*

Swati Sinha and J. N. Bardsley†

Physics Department, University of Pittsburgh, Pittsburgh, Pa. 15260

and

Joint Institute for Laboratory Astrophysics

University of Colorado and National Bureau of Standards

Boulder, CO. 80302

Abstract

Previous calculations of ion-atom interactions by the pseudopotential and asymptotic methods are used in the computation of the cross section for symmetric charge transfer at energies below 1 keV. The results for Li^+, Na^+, K^+, Rb^+, Cs^+ and Ca^+ ions are compared with data obtained in beam experiments, and by optical pumping techniques. The difference in the cross sections for $^2P_{1/2}$ and $^2P_{3/2}$ ions of Kr^+ and Xe^+ at thermal energies is studied and the predictions are compared with recent mobility measurements. Cross sections are obtained for U^+ - U collisions, and the dependence of the thermal cross section on the polarizability is described. Symmetric charge transfer of the negative ions H^-, Na^- and Cs^- is discussed briefly.

*This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR under Contract No. N00014-76-C0098, and by ERDA under Contract No. E(04-3)-1106.

†JILA Visiting Fellow 1974-75.

1. Introduction

For many years there has been considerable interest in symmetric charge transfer reactions at low energies. This is due in part to the fact that the large cross sections for this process lead to a considerable reduction in the mobility of ions in their parent gases. Also a simple theoretical model of the process has been developed[1-14] which shows that the magnitude of the cross section is controlled mainly by the long range interactions, which can be computed using asymptotic theories. Thus it is possible that the calculated cross sections may be more accurate than is typical for ionic collision processes.

The reaction can be expressed symbolically as

$$X^+ + X \rightarrow X_2^+ \rightarrow X + X^+ \quad . \tag{1}$$

At very low energies we can consider the formation and dissociation of the molecular ion to occur adiabatically, that is without any change in the molecular electronic state. The simplest situation arises when the initial states of the ion and atom are in S - states and one of them has zero spin (e.g. X ≡ H, He, Li, Be, Au, Hg). For such systems two molecular states are involved; asymptotically these states correspond to gerade and ungerade linear combinations of the initial and final states in reaction (1). The crucial step in the calculation is the computation of the potential curves of these states, $E_g(R)$ and $E_u(R)$, at large internuclear distances.

Although the theory can be formulated completely in terms of quantum mechanics, the impact parameter approximation can be used without significant loss of accuracy. In this approach one considers the nuclei

to move along classical trajectories determined by the molecular potential energy curves. The cross section is then written as

$$Q(v) = 2\pi \int_0^\infty P(b,v)\, b^2 db \quad . \tag{2}$$

P(b,v) denotes the probability that charge transfer will take place during a collision with impact parameter b and relative velocity v, and can be expressed in terms of the phase shifts, $\eta_g(b,v)$ and $\eta_u(b,v)$, for scattering along the molecular potential curves $E_g(R)$ and $E_u(R)$.

$$P(b,v) = \sin^2[\eta_u(b,v) - \eta_g(b,v)] \tag{3}$$

This phase difference can be computed using the JWKB approximation,

$\Delta\eta(b,v) = \eta_u(b,v) - \eta_g(b,v) =$

$$\int_{R_{og}}^{\infty} \left[2m\left\{E\left(1 - \frac{b^2}{R^2}\right) - E_g(R)\right\}\right]^{\frac{1}{2}} dR - \int_{R_{ou}}^{\infty} \left[2m\left\{E\left(1 - \frac{b^2}{R^2}\right) - E_u(R)\right\}\right]^{\frac{1}{2}} dR \tag{4}$$

Here E is the collision energy in the center-of-mass coordinate frame, m is the reduced mass, and R_{og} and R_{ou} are the classical turning points for the motion along the two potential curves. Note that we do not need to assume straight line paths or even a common trajectory.

For low energy collisions the charge transfer probability P(b,v) oscillates rapidly between 0 and 1 for values of b less than some value b_o, and then decreases exponentially for $b > b_o$. This behaviour led Firsov[2] to suggest a very simple approximation for the integral over impact parameter in Eq. (2). For $b < b_o$, Firsov replaced P(b,v) by its average value of $\frac{1}{2}$, whereas for $b > b_o$ he set P(b,v) equal to zero. The charge transfer cross section is then equal to $\frac{1}{2}\pi b_o^2$. The parameter b_o is defined to be the highest impact parameter at which P(b,v) attains a

critical value, P_o, which Firsov took to be close to 0.1. Rapp and Francis[7] used the same procedure but with P_o equal to 0.25, whereas Smirnov[8,9] took P_o to be about 0.075 and used a slightly different approximation for the integral. In each of these theories straight line trajectories were assumed and the results were expressed in the form

$$Q^{\frac{1}{2}}(v) = A - B \log v \qquad (5)$$

in which A and B are constants which are determined mainly by the ionization potential of the atom involved in the collision.

For systems in which there is degeneracy in the initial states we must consider more than two molecular states. For example, in the interaction of a ^1S atom with a ^2P ion we obtain Σ states and Π states. For such cases we must compute two phase differences for each value of b and v, once using the Σ- state curves and once using the Π- state curves. We will assume that during the collision the different molecular states are populated in proportion to their statistical weights.

In a previous paper[15] we have discussed the asymptotic method for computing the potential energy curves, $E_g(R)$ and $E_u(R)$, at large values of R for positive ion systems in cases where fine-structure splittings are insignificant. In sec. II we will summarize the results of that paper and will examine the effects arising from the spin-orbit splittings.

In secs. III and IV we will describe calculations of the cross sections for resonant charge transfer of Li^+, Na^+, K^+, Rb^+, Cs^+ and Ca^+ ions and will compare the results with experiment. We will also present results for U^+ - U collisions, for which we are aware of no published experimental data.

Recent experiments by Helm[15] on the drift motion of Kr^+ ions in Kr gas have shown that there is a difference of about 3% in the mobilities of the $^2P_{3/2}$ and $^2P_{1/2}$ fine-structure components of the ionic ground state. In Sec. V we will examine the cross sections for resonance charge transfer for both ionic states to see if there is a similar difference. A similar, but larger, effect is found for Xe^+ drifting through Xe[17].

Our major aim in this paper is to exploit the results of the asymptotic theory of ion-atom interactions. Thus we will concentrate on the energy region below 1 keV in which the cross sections are large. The charge transfer cross sections all show a decreasing trend as the energy increases, but in the energy range above 100 eV there are often small oscillations. These oscillations arise from collisions with relatively small impact parameters, so that their form depends critically on the behaviour of the potential curves at small distances. Hence we will not attempt to predict the amplitude and shape of the oscillations.

We will also attempt to check some of the approximations which were made in the early theories[2-14] in order to obtain analytic expressions for the cross sections.

If the asymptotic method is applied to the resonant charge transfer of negative ions, and if the effects of polarization are neglected, the result is similar to that obtained by Smirnov and Firsov[18] using the zero-range-potential method. One finds a strong correlation between the charge transfer cross section and the atomic electron affinity. Bydin[19] has measured the charge transfer cross sections for the alkali ions Na^-, K^-, Rb^- and Cs^-, and has deduced values of the electron affinities of these ions by application of the Smirnov-Firsov theory. The values predicted in this way are not consistent with the results of the recent laser photodetachment experiments[20]. For example, Bydin deduced the

value of 0.13 ± 0.07 eV for the electron affinity of Cs whereas the measured value is 0.471 ± .003 eV. In spite of the more recent theoretical work of Davidovic and Janev[21] it is unclear whether this discrepancy arises from errors in the theory or in the experiment.

Thus it was our original intention to perform accurate calculations for some negative ion systems in order to check the accuracy of Bydin's experimental work. However, there are serious difficulties in estimating the long-range interactions of negative ions with atoms which have a high polarizability, and there are no reliable ab initio calculations of such interactions. Nevertheless we were able to reach some conclusions about the experimental results. In Sec. VI we will discuss these theoretical problems and will summarize our findings.

Atomic units will be used in the equations of this paper, but cross sections will be presented in units of $\AA^2$, with energies specified in eV.

2. Asymptotic theory of ion-atom interactions

The long-range interaction between an ion and its parent atom can be expressed in the form

$$E(R) \approx E(\infty) - \frac{\alpha}{2R^4} \pm \tfrac{1}{2}\Delta E(R) \qquad (6)$$

Here α is the polarizability of the neutral atom and $\Delta E(R)$ is the exchange splitting which arises because of the indistinguishability of the electrons in the system. In our earlier paper[15] we discussed the computation of $\Delta E(R)$ for positive ion systems in which the spin-orbit forces are negligible. We assume that the electrons of the ion and atom move in independent orbitals, and that the atomic wave function is constructed from the orbitals of the ion together with one additional orbital to describe the electron which is transferred . The exchange splitting $\Delta E(R)$ is then determined

by the quantum numbers, ℓ, m, and size of this latter orbital. If the ionization potential, I, is written as $1/(2\nu^2)$ then the asymptotic form of $\Delta E(R)$ is

$$\Delta E_{\ell m}(R) = (-)^m + N_i \; A \; R^{2\nu-1-m} \exp\left(\frac{-R}{\nu}\right)\left[1 + \frac{B}{R} + O\left(\frac{1}{R^2}\right)\right] \quad (7)$$

Here m denotes the component of the orbital angular momentum, ℓ, about the inter-nuclear axis, and N_i is the number of equivalent electrons in the outer shell of the ion. The constants A and B depend on ν, ℓ and m and A also depends on the normalization constant in the orbital corresponding to the transferred electron. The determination of this normalization constant is the major uncertainty in the application of the asymptotic method[15].

The sign and relative magnitude of $\Delta E_{\ell m}(R)$ should be specially noted. When N_i is even, as in H_2^+ and Li_2^+, Σ_u states lie above the Σ_g states which dissociate to the same limit, whereas Π_g states are above Π_u states. When N_i is odd, as in He_2^+ and Ne_2^+, these orderings are reversed. In cases where both Σ and Π states share a common dissociation limit, such as B_2^+ and Ne_2^+, the Σ splittings are greater than the Π splittings.

When fine structure splittings are significant we must specify the total angular momentum j of the active electron orbital and its component Ω along the internuclear axis. We will later examine the molecular ions Kr_2^+, Xe_2^+ and U_2^+ at sufficiently large values of R that the spin-orbit splittings are large compared to $\Delta E(R)$. We can then assume that the matrix elements of the spin-orbit interaction are independent of R.

One can easily show that in this situation

$$\tilde{\Delta E}_{j\Omega}(R) = \sum_{\mu m} (C \begin{matrix} \ell & \frac{1}{2} & j \\ m & \mu & \Omega \end{matrix})^2 \Delta E_{\ell m}(R) \qquad (8)$$

We have used the tilde to indicate that the splittings refer to the $(j\Omega)$ representation. In applying Eq. (8) one should clearly take account of the sign of $\Delta_{\ell m}(R)$ and Duman and Smirnov[12] appear to have neglected the variation of this sign in their study of the inert gas systems. This mistake was not made by Johnson[11].

III. Results for alkali positive ions

The positive ions of the alkali atoms are particularly suitable for tests of the two-state model of the resonant charge transfer process. In our previous paper[15] we have computed the asymptotic form of the energy splitting $\Delta E(R)$. For intermediate separations, between 2 and 20 a.u. the splittings were obtained by the pseudopotential method[15,23]. There is some uncertainty in the splittings at smaller distances, especially for the heavier alkali ions. The potential curves in this latter region influence the form of the oscillations in the cross sections. We will discuss the oscillations only for the case of Li^+, since ab initio potential curves are available for Li_2^+ at small separations.

Let us first consider the major sources of error in the two-state model for Li^+ - Li collisions. Firstly there is a crossing between the lowest $^2\Sigma_u$ and $^2\Pi_u$ curves of Li_2^+ at around 5.6 a.u.[24] that will lead to excitation of the Li atom to the lowest ^2P state. This crossing could possibly produce oscillations of amplitude up to 10 A^2 in the charge transfer cross sections. At a separation of around 0.6 a_o there is an avoided crossing between the lowest two $^2\Sigma_u$ states, and the lowest one crosses below the $^2\Sigma_g$ curve as the united atom limit is approached. These latter

effects will lead to a small modification of the charge transfer cross section above 100 eV. Finally, at energies above a few keV the molecular approach will be less useful as non-adiabatic effects become important.

We have estimated the g-u splitting for separations down to zero and have computed the charge transfer probability P(b) for all b. The cross section was then obtained by numerical integration. In Fig. 1 the computed cross section is presented as a function of inverse velocity for center-of-mass energies between 200 and 2000 eV. One does see oscillations which appear to have a constant wavelength on this plot, in agreement with the theory of Smith[25-27]. The oscillations are primarily due to the maximum in the energy difference $\Delta E(R)$ which occurs around R = 4 a.u. Fig. 1 also includes the experimental results of Perel et al.[28] and the results of two-state calculations by McMillan[29]. The most obvious discrepancy is that both theoretical results are approximately 15% higher than the measured values. This difference was also found in the previous two-state calculations by Bottcher et al[30]. The oscillations in each of the theoretical cross sections are approximately of the same size as in the experimental results but there are significant differences in the positions of the peaks. McMillan[29] has shown that allowance for the coupling of the $^2\Sigma_u$ and $^2\Pi_u$ states leads to a shift in the positions of these peaks and improves the agreement with experiment. However, the magnitude of the computed cross section is not changed significantly by the introduction of the third state.

In Fig. 2 we present our results over a wide range of energies in an alternate form, with $(Q)^{\frac{1}{2}}$ plotted against log E. Between 0.25 eV and 50 eV we find the linear behaviour predicted by the Firsov theory. Above 50 eV the linear law describes the general trend but the small oscillations are apparent. Below 0.25 eV the cross section is increased

because of the polarization attraction. However at the thermal energy of 0.025 eV our value of 364Å^2 is significantly higher than the Langevin limit of $\pi(\alpha/2E)^{\frac{1}{2}}$. Fig. 2 also includes the experimental results of Lorents et al[31], and the theoretical results of Dumen and Smirnov[11].

The theoretical results are in good agreement for energies above 1 eV, thus confirming the validity of the approximations used by Duman and Smirnov. At lower energies our cross sections are higher, since we allowed for the bending of the trajectories due to the attractive polarization force. Although the theoretical and experimental curves intersect at around 200 eV there is a significant discrepancy in the energy dependence of the cross section. For a center-of-mass energy of 7 eV our computed value of ~ 175Å^2 is over 25% smaller than the experimental value of 240Å^2. This difference is considerably larger than the experimental error of 8%, as estimated by Lorents et al.

For Na^+-Na collisions at energies above 500 eV our computed cross sections are about 15% above the experimental values of Daley and Perel[32], but are close to the previous two-state calculations by Bottcher et al[30]. Once again the magnitude and frequency of the oscillations are predicted well by the theory, but there is a discrepancy in the phase of the oscillations. We believe that this is due predominantly to our neglect of the $^2\Pi_u$ state of Na_2^+ which crosses the $^2\Sigma_u$ state around 5 a.u.[22,30]. Some of our calculated values are given in Table I.

Our results for the heavier alkalis K^+, Rb^+ and Cs^+ are presented in Table I, and in Figs. 3-5 they are compared with the values obtained in recent experiments. Gentry, Lee and Mahan[33] have performed beam experiments for each of these ions at laboratory energies between 10 and 500 eV. Once again the experimental results decrease more rapidly than the calculated values. For Rb^+ and Cs^+ theory and experiment are in good

agreement for laboratory energies around 20 eV. Measurements have been made for these two ions at higher energies by Perel et al[27,34]. For laboratory energies near 1 keV their measured cross sections are 15-20% below our computed values. The cross sections measured by Gentry et al.[33] for K^+ charge transfer are considerably lower than our calculated values. However the authors expressed some uncertainty regarding the absolute magnitude of their potassium cross sections.

Mitchell and Fortson[35] have measured the charge transfer cross sections for Rb^+ and Cs^+ at thermal energies in an optical-pumping experiment. For Rb^+ our calculated value of $569 A^2$ is barely consistent with their measured value of $710 \pm 150\ A^2$, whereas in Cs^+ our value of $650\ A^2$ is well within their limits of $800 \pm 300\ A^2$. For Cs^+ a lower cross section was reported in a similar experiment by Oluwole and Togun[36]. However we believe that there may have been an error in the analysis of their experiment.

Andersen et al.[37] have recently studied Cs^+-Cs charge transfer in a Q- machine and obtained a value of $600 \pm 200 \mathring{A}^2$ for incident ion energies of 2 eV. Our computed value of $450\ A^2$ falls once again in the lower portion of this range.

Calculations similar to ours have been performed by Smirnov[7] with results that are smaller by about 10%. However the more recent paper by Duman and Smirnov[13] seems to indicate that there were some errors in the earlier work and the values quoted in this latter paper are very close to our results for laboratory energies of above 1 eV. However their assumption of straight line trajectories again leads to a significant underestimation of the cross section at very low energies.

IV. Results for Ca^+ and U^+

Two recent measurements of Ca^+-Ca charge transfer cross sections have given widely different results. Rutherford et al.[38] obtained a cross section which decreases from 550 A^2 at 3 eV to 320 A^2 at 500 eV, whereas the cross section measured by Panev et al.[39,40] decreases from 220 A^2 at 6 eV to 160 A^2 at 1000 eV.

For atoms such as Ca, with two valence electrons, the determination of the asymptotic normalization constant q (defined in Eq. 2 of Ref. 15) is especially difficult. From an examination of the multi-configuration ground state wave functions obtained by Robb[41] we were able to deduce only that q probably lies between 1.0 and 1.5. The value deduced by Duncan and Smirnov by fitting to a single-configuration Hartree-Fock wave function was 1.0. Hence we have performed calculations of the cross section with q set equal to 1.0 and 1.5. As can be seen from Fig. 6, the values measured by Panev et al.[39,40] fall close to the results we obtain with q = 1.5, whereas the measurements of Rutherford et al.[38] are well outside the range of our results. The calculations of Duman and Smirnov lie slightly below the results that we obtain with q = 1.

The oscillations in the observed cross sections[39,40] extend to much lower energies than in the alkali systems. We support the suggestion of Panev et al. that this indicates the existence of a curve crossing at a relatively large internuclear separation.

The valence structure of the uranium atom is $(5f_{5/2})^3\ (7s_{1/2})^2\ (6d_{3/2})$, and the ground state of the positive ion is obtained by removing the $6d_{3/2}$ electron. Although the 5f shell is not filled the $5f_{5/2}$ orbital is significantly smaller than both the $7s_{1/2}$ and $6d_{3/2}$ orbitals. Thus we will assume that the coupling between the $5f_{5/2}$ and $6d_{3/2}$ electrons is not important and apply the one-electron model,

assuming transfer of the $6d_{3/2}$ electron. The spin-orbit forces are sufficiently strong that we must compute the molecular splittings using the j-Ω representation. Following the method outlined in Sec. II we find that

$$\Delta E_{3/2\ 3/2} = \frac{4}{5}\Delta E_{22} + \frac{1}{5}\Delta E_{21} \tag{9}$$

$$\tilde{\Delta E}_{3/2\ 1/2} = \frac{3}{5}\Delta E_{21} + \frac{2}{5}\Delta E_{20}$$

In writing down the asymptotic form of the $6d_{3/2}$ orbital, we chose the normalization constant q to be 0.4 in order to reproduce the expectation value $\langle r^4 \rangle$ found in the relativistic Hartree-Fock calculations by Mann[42].

At thermal energies the polarization attraction leads to significant bending of the trajectories. Unfortunately the polarizability of U is not known. Using the oscillator strength sum rule we estimate the polarizability to be 162 a.u. but we have also performed calculations using the values of 120 a.u. and 200 a.u. As can be seen from Fig. 7 the effect of polarization is insignificant for energies of relative motion above 2 eV.

For values of the center-of-mass energy E between 0.025 eV and 100 eV our results with a polarizability of 162 a.u. are well fitted by the form

$$Q = (12.6 - 1.55 \log_{10} E)^2 + 1.153\ E^{-1.12} \tag{10}$$

if E is expressed in eV and Q in $\mathring{A}^2$. For a center-of-mass energy of 0.025 eV the dependence of the cross section on the polarizability can

be approximated by

$$Q = 240\left[1 + \left(\frac{\alpha}{136.7}\right)^2\right]^{1/4} \qquad (11)$$

if α is expressed in a.u., and Q in $\mathring{A}^2$.

V. Effects of the fine-structure splittings in Kr^+ and Xe^+

Helm[16] has recently reported studies of the drift motion of Kr^+ ions in a buffer gas of Kr atoms, in which he was able to make separate measurements of the mobilities of the lowest $^2P_{3/2}$ and $^2P_{1/2}$ states of Kr^+. He found that the mobility of the metastable $^2P_{1/2}$ state is higher than that of the ground state by $3.3 \pm 0.2\%$ for swarms of ions with characteristic energies between 0.03 and 0.04 eV. For Xe^+ in Xe he finds a difference of about 6%[17].

Ionic mobility is primarily determined by the momentum-transfer cross section for collisions of the ions with the buffer gas atoms and in the zero field limit one can obtain a simple expression for the mobility[43]. Furthermore it is usually assumed that the momentum transfer cross section for ions colliding with their parent gas atoms is approximately equal to twice the charge transfer cross section.

The values of the cross sections on which these estimates are based are given in Table II. Thus one might expect the charge transfer cross sections for $^2P_{3/2}$ and $^2P_{1/2}$ ions to be different by amounts equal to those quoted above.

For ion energies of around 1 keV the experimental work of Hishinuma[44] and the calculations by Kimura and Watanabe[45] and by Johnson[46] suggest that the difference in the charge transfer cross sections of the two states is about 10% for Kr^+ and 15% for Xe^+. The experimental results[44] show the difference to be increasing as the energy is reduced. However at very low energies the cross section should be determined solely by the

polarizability of the neutral atom and the energy, and so should be independent of the ionic state. This expectation is consistent with the calculations by Johnson[46] and by Cohen and Schneider[47]. Thus it seemed worthwhile to examine the charge transfer cross sections for Kr^+ and Xe^+ at the energies appropriate to the drift tube experiments.

For ions with J = 3/2 the component of angular momentum about the nuclear axis, Ω, can be either 1/2 or 3/2. The charge transfer cross section can then be obtained by averaging over the cross sections appropriate to collisions with Ω = 1/2 and Ω = 3/2. For J = 1/2, on the other hand, we can have only Ω = 1/2 so that no averaging is needed. The energy splittings appropriate to each set of values of J and Ω can be obtained by using Eqs. (7) and (8). It should be noted that in applying these equations one does not have to assume that the $p_{1/2}$ and $p_{3/2}$ electron orbitals have the same dependence on the radial coordinate r.

The asymptotic normalization constants q were obtained by fitting to the relativistic Dirac-Fock wave functions of Desclaux[48]. The resulting cross sections are tabulated in Table 2 and Figs. 8-9. Even at an energy of 0.01 eV the cross section does depend upon J but the differences are significantly less than those found at higher energies.

We have computed the zero-field limit of the reduced mobility, assuming that the momentum-transfer cross section is exactly twice the charge transfer cross sections. For Kr^+ ions at a temperature of 300°K we obtain values of 0.896 $cm^2\ V^{-1}\ sec^{-1}$ for $^2P_{3/2}$ ions and 0.913 $cm^2\ V^{-1}\ sec^{-1}$ for $^2P_{1/2}$ ions. The difference of 1.8% is smaller than the 3.3% difference observed by Helm[16]. The absolute values are consistent with the experimental results to better than 5%.

For Xe^+ in Xe our calculated mobilities are 0.562 $cm^2\ V^{-1}$ for $^2P_{3/2}$ ions and 0.597 $cm^2\ V^{-1}\ s^{-1}$ for $^2P_{1/2}$ ions. By extrapolation

of the experimental data to zero field Helm[17] obtains the values $0.532 \pm .003$ $cm^2\ V^{-1}\ s^{-1}$ and $0.563 \pm .003$ $cm^2\ V^{-1}\ s^{-1}$ respectively. The mobility ratio is thus in very good agreement.

The experimental errors in measurements of the mobility are very small compared to those associated with direct studies of charge transfer cross sections. The drift tube may therefore provide the most precise technique for the measurement of these cross sections at low energies, and thus further examination of the dependence of the mobility upon the rate of charge transfer would be worthwhile.

Our cross sections for Kr^+ are considerably smaller than those measured in an ion-cyclotron-resonance experiment by Smith and Futrell[49]. By injecting ions into a drift tube Kobayashi and Kaneko[50] studied Kr^+-Kr charge transfer over a range of energies from 0.04 eV to 3 eV. They found the cross section to be independent of energy with a value of $100 \pm 15 \mathring{A}^2$. Our calculations predict a cross section of $100\ \mathring{A}^2$ at the lower end of this range but at 3 eV we would estimate the cross section to be about $60 \mathring{A}^2$.

VI. Symmetric charge transfer for H^-, Na^- and Cs^-

In the charge exchange of negative ions the transferred electron initially belongs to the ion, X^-. In the simplest approximation, its wave function in the asymptotic region can be written in the form

$$u_o(r) = q \frac{1}{r} e^{-\zeta r} Y_\ell^m (\Omega) \qquad (12)$$

where ζ is such that the electron affinity is equal to $\frac{1}{2}\zeta^2$. The perturbing system is now a neutral atom, X, and one argues that at large internuclear separations the distortion of this electronic wave function by the approaching atom is negligible. One can then build up orbitals for

the molecular ion, X_2^-, from linear combinations of two atomic orbitals of the form (12), and compute the splitting between the gerade and ungerade potential curves just as one does for positive ions. The theory is then equivalent to the zero-range-potential (ZRP) method used by Smirnov and Firsov[18], except that the constant q need not be assigned the value given by those authors.

Bydin[19] used the ZRP theory in order to deduce electron affinities for Na, K, Rb and Cs from his measurements of the charge transfer cross sections, obtaining values that are significantly lower than the values obtained later in high-resolution photodetachment experiments[20]. Part, but not all of the discrepancy can be attributed to his choice of values for the constant q.

One obvious deficiency in the ZRP approach is that no account is taken of polarization effects, which might be important for alkali systems. Using the JWKB approximation one can easily amend eq. (12) to allow for polarization effects within an undistorted ion. For example, for S states one finds that for large r

$$u_0(r) \approx \frac{1}{4\pi} \; q \; \frac{1}{r} \; \exp\left[- \zeta r - \frac{\alpha}{6\zeta r^3} + \frac{\alpha}{4\zeta^2 r^4} \right] \qquad (13)$$

in which α is the polarizability of the neutral atom. However allowance for the distortion of this orbital due to the polarization interaction with the approaching neutral atom is more difficult. We have been able to do this only by assuming that there exists a range of values of r which are large enough so that (13) is a valid representation of $u_0(r)$ but are small enough that there is insignificant distortion due to the neighbouring atom. Such a region can exist only for large values of the inter-nuclear distance, say $R \gtrsim 20$ a.u. In applying this theory we

found that the polarization interactions do not lead to significant changes in the cross section, except perhaps through their influence on the value of the constant q. Thus, although we have performed calculations for Na^- and Cs^-, we do not deem it worthwhile to describe in detail our theoretical method, or to give quantitative results. Nevertheless we can state with some confidence that the magnitude of the cross sections measured by Rydin for Cs^- - Cs collisions seem to be consistent with the one-electron model whereas his values for Na^- - Na are only about 40% of the cross sections predicted by the model. Once again the experimental cross sections decrease more rapidly than the theoretical results as the energy is increased.

The cross sections given by Duman and Smirnov for Na^-, K^-, Rb^- and Cs^- appear to be much too large due to the use of incorrect values for the electron affinity.

At thermal energies the cross sections should be predicted well by the ZRP model, provided that ζ and q are chosen correctly. For a center-of-mass energy of 0.025 eV we find cross sections of 225$\mathring{A}^2$, 910$\mathring{A}^2$ and 1320$\mathring{A}^2$ for H^- - H, Na^- - Na and Cs^- - Cs collisions, respectively. These cross sections are so large that the effects of curvature in the trajectories are negligible, which is perhaps surprising at such a low energy.

VII. Conclusions

The cross sections that we have reported were obtained by numerical evaluation of the JWKB phase shifts and numerical integration of the probability of charge transfer over the impact parameter. Many authors have previously suggested approximate techniques by which the cross sections can be derived analytically. In particular there is a

comprehensive tabulation of cross sections by Duman and Smirnov[13], and there are some very recent calculations by Hodgkinson and Briggs[14].

For three of the systems discussed above, we tested the validity of the Firsov procedure of setting the integral of P(b,v) over b equal to $\frac{1}{2}\pi b_o^2$. For Rb^+ and Ca^+ we find that if the critical parameter b_o is chosen in the manner suggested by Smirnov, namely the largest value of b for which $\Delta\eta(b,v)$ is equal to 0.275, then the cross sections are predicted with an error of around 1%. For Cs^- the error seems to have a constant value of around 10Å^2. This critical value corresponds to a charge transfer probability of ~ 0.075. The critical values suggested by Firsov[2] and by Rapp and Francis[7] do not lead to such good results.

The major errors in the cross sections tabulated by Duman and Smirnov[13] arise from the assumption of straight line trajectories, which in most cases is not justified for an energy of 0.1 eV. Most of their values at this energy are therefore significantly too small. All our cross sections seem to be higher than those of Duman and Smirnov, but at energies of 1 eV and above the differences are less than 10%, except for Kr^+ - Kr collisions. For that system we believe that the results quoted by Duman and Smirnov should be increased by approximately 75%. Our results are also close to, but slightly higher than, those obtained by Hodgkinson and Briggs[14].

We have shown that for Kr^+ ions and Xe^+ ions the cross sections for charge transfer are different for the two fine-structure components of the ground state. The different mobilities that have been found for $^2P_{1/2}$ and $^2P_{3/2}$ ions of Kr^+ and Xe^+ moving through their parent gas atoms may therefore be attributed to the different charge transfer cross sections. However although theory and experiment agree on the size of this effect in Xe, there is a discrepancy in Kr which we do not understand.

There seems to be a systematic difference in the energy dependence of the cross sections for symmetric charge transfer between theory and experiment, with a more rapid decrease being seen in the experimental data. Further theoretical study and more accurate beam data may therefore be worthwhile.

We believe that the most reliable information concerning symmetric charge transfer comes from mobility measurements, and thus intend to study the transport theory more carefully to determine the accuracy with which cross sections can be derived from such data.

Acknowledgements

We are grateful to Drs. H. Helm, B. R. Junker, J. B. Mann, D. W. Norcross and W. D. Robb for the provision of unpublished information and to Dr. Yu. N. Demkov for his interest and advice throughout this work.

References

1. H. S. W. Massey and R. A. Smith, Proc. R. Soc. Lond. A142, 142 (1933).
2. O. B. Firsov, Zh. Eksp. Teor. Fiz. 21, 1001 (1951).
3. Yu. N. Demkov, Uchen. Zap. Leningr. Gos. Univ. 146, 74 (1952).
4. T. Holstein, J. Phys. Chem. 56, 832 (1952).
5. E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26, 1237 (1957).
6. A. Dalgarno, Phil. Trans. Roy. Soc. A250, 426 (1958).
7. D. Rapp and W. E. Francis, J. Chem. Phys. 37, 2631 (1962).
8. B. M. Smirnov, Zh. Eksp. Teor. Fiz. 46, 1017 (1963) [Sov. Phys. - JETP 19, 692 (1964)], Zh. Eksp. Teor. Fiz 47, 518 (1964) [Sov. Phys. - JETP 20, 345 (1965)]; B. M. Smirnov and M. I. Chibisov, Zh. Tech. Fiz. 35, 115 (1965) [Sov. Phys. Tech. Phys. 10, 88 (1965)].
9. B. M. Smirnov, Teplofiz. Vys. Temp. 4, 429 (1966) [High Temp. 4, 407 (1966)].
10. E. L. Duman and B. M. Smirnov, Zh. Tekh. Fiz. 40, 91 (1970) [Sov. Phys.-Tech. Phys. 15, 61 (1970)].
11. R. E. Johnson, J. Phys. B 3, 539 (1970).
12. E. L. Duman and B. M. Smirnov, Opt. Spektrosk. 32, 448 (1971) [Opt. Spectrosc. 32, 234 (1972)].
13. E. L. Duman and B. M. Smirnov, Teplofiz. Vys. Temp. 12, 502 (1974) [High Temp. 12, 431 (1975)].
14. D. P. Hodginkson and J. S. Briggs, J. Phys. B. 9, in press (1976).
15. J. N. Bardsley, T. Holstein, B. R. Junker and S. Sinha, Phys. Rev. A11, 1911 (1975).
16. H. Helm, Chem. Phys. Lett. 36, 97 (1975).
17. H. Helm, Amer. Phys. Soc. Bull. 20, in press (1976); and private communication.

18. B. M. Smirnov and O. B. Firsov, Zh. Eksp. Teor. Fiz. 47, 232 (1964) [Sov. Phys. - JETP 20, 156 (1965)].

19. Yu. F. Bydin, Zh. Eksp. Teor. Fiz. 46, 1612 (1964)[Sov. Phys. - JETP 19, 1091 (1964)].

20. T. A. Patterson, H. Hotop, A. Kasdan, D. W. Norcross and W. C. Lineberger, Phys. Rev. Lett. 32, 189 (1974).

21. D. M. Davidovic and R. K. Janev, Phys. Rev. 186, 89 (1969).

22. J. N. Bardsley, B. R. Junker and D. W. Norcross, Chem. Phys. Lett., in press (1976).

23. J. N. Bardsley, Case Studies in Atomic Physics, 4, 299 (1974).

24. J. N. Bardsley, Phys. Rev. A3, 1317 (1971).

25. F. J. Smith, Phys. Letters 20, 271 (1966).

26. J. Perel, Phys. Rev. A1, 369 (1970).

27. J. Perel, H. L. Daley and F. J. Smith, Phys. Rev. A1, 1626 (1970).

28. J. Perel, H. L. Daley, J. M. Peek and T. A. Green, Phys. Rev. Lett. 23, 677 (1969).

29. W. McMillan, Phys. Rev. A4, 69 (1971).

30. C. Bottcher, A. C. Allison and A. Dalgarno, Chem. Phys. Lett. 11, 307 (1971).

31. D. C. Lorents, G. Black and O. Heinz, Phys. Rev. 137, A1049 (1965).

32. H. L. Daley and J. Perel, Abstr. 6th Int. Conf. on the Physics of Electronic and Atomic Collisions (MIT Press, Cambridge, Mass., 1969) p. 1051.

33. W. R. Gentry, Y-T. Lee and B. H. Mahan, J. Chem. Phys. 49, 1758 (1968).

34. J. Perel, R. H. Vernon and H. L. Daley, Phys. Rev. A 138, 957 (1965).

35. J. K. Mitchell and E. N. Fortson, Phys. Rev. A8, 704 (1973).

36. A. F. Oluwole and E. A. Togun, J. Phys. B 6, L334 (1973).

37. S. A. Andersen, V. O. Jensen and P. Michelsen, Rev. Sci. Inst. 43, 945 (1972).

38. J. A. Rutherford, R. F. Mathis, B. R. Turner and D. A. Vroom, J. Chem. Phys. 57, 3087 (1972).

39. G. S. Gaev and O. B. Shpenik, Zh. Eksp. Teor. Fiz. Pis. Red 19, 209 (1974) (JETP Lett. 19, 128 (1974)).

40. G. S. Panev, A. N. Zavilopulo, I. P. Zapesochnyi and O. B. Shpenik, Zh. Eksp. Teor. Fiz. 67, 47 (1974) (Sov. Phys. JETP 40, 23 (1974)).

41. W. D. Robb, private communication.

42. J. B. Mann, private communication.

43. E. W. McDaniel and E. A. Mason, The Mobility and Diffusion of Ions in Gases (Wiley, New York, 1973).

44. N. Hishinuma, J. Phys. Soc. Japan 32, 227 (1972); 32, 1452 (1972).

45. M. Kimura and T. Watanabe, J. Phys. Soc. Japan 31, 1600 (1971).

46. R. E. Johnson, J. Phys. Soc. Japan 32, 1612 (1972).

47. J. S. Cohen and B. Schneider, J. Chem Phys. 61, 3230 (1974); Phys. Rev. A 11, 884 (1975).

48. J. P. Desclaux, Atomic Data and Nuclear Data Tables 12, 311 (1973).

49. D. L. Smith and J. H. Futrell, J. Chem. Phys. 59, 463 (1973).

50. N. Kobuyashi and Y. Kurako, J. Phys. Soc. Japan 34, 496 (1973).

Figure Captions

Fig. 1 Charge transfer cross sections for Li^+ - Li collisions as a function of the inverse velocity, O this work, X two state calculations of McMillen[29], Δ experimental results of Perel et al.[28]

Fig. 2 Square root of the Li^+ - Li cross section as a function of the center-of-mass energy, — this work, Δ Duman and Smirnov[13] (theory), _ _ Lorents et al.[31] (expt.).

Fig. 3 K^+ - K charge transfer cross sections as a function of center-of-mass energy, _____ this work, _ _ Duman and Smirnov[13] (theory), O Gentry et al.[33] (expt.).

Fig. 4 Rb^+ - Rb cross sections, showing the values calculated in this work (full line) and by Duman and Smirnov[13] (long-dashed line), and the experimental results of Gentry et al.[33] (circles) and Perel et al.[27,34] (short-dashed line).

Fig. 5 Cs^+ - Cs cross sections, with the same notation as in Fig. 4.

Fig. 6 Ca^+ - Ca cross sections. The dashed lines show the theoretical results obtained in this work with q = 1.5 (A) and q = 1.0 (B) and by Duman and Smirnov (C); the experimental results of Rutherford et al.[38] (circles) and Panev et al.[39,40] (full line) are also shown.

Fig. 7 Square root of the U^+ - U cross sections for three values of the polarizability, X 120 a.u., O 162 a.u, Δ 200 a.u.

Fig. 8 Square root of the Kr^+ - Kr cross section, for both $^2P_{3/2}$ and $^2P_{1/2}$ ions.

Fig. 9 Square root of the Xe^+ - Xe cross section, for both $^2P_{3/2}$ and $^2P_{1/2}$ ions.

Table I. Charge transfer cross sections, in $\mathring{A}^2$, for alkali ions

E_{CM}	Li^+	Na^+	K^+	Rb^+	Cs^+
0.025	346	388	520	569	650
0.05	302	345	461	514	590
0.1	273	318	424	476	543
0.5	230	269	364	411	475
1	215	254	344	389	450
5	182	220	301	341	397
10	169	206	282	323	376
20	156	193	266	303	354
50	140	175	243	280	328
100	127	163	228	269	308
200	116	153	212	250	289
500	111	135	192	223	264

Table II. Charge Transfer cross sections, in $\mathring{A}^2$, for Kr^+-Kr and Xe^+-Xe

	Kr^+		Xe^+	
E_{CM}	$^2P_{3/2}$	$^2P_{1/2}$	$^2P_{3/2}$	$^2P_{1/2}$
0.01	140	138	180	173
0.02	114	112	145	139
0.05	93.0	91.3	119	112
0.1	83.8	81.6	107	100
0.2	76.9	75.1	98.3	91.5
0.5	69.4	67.9	89.6	82.9

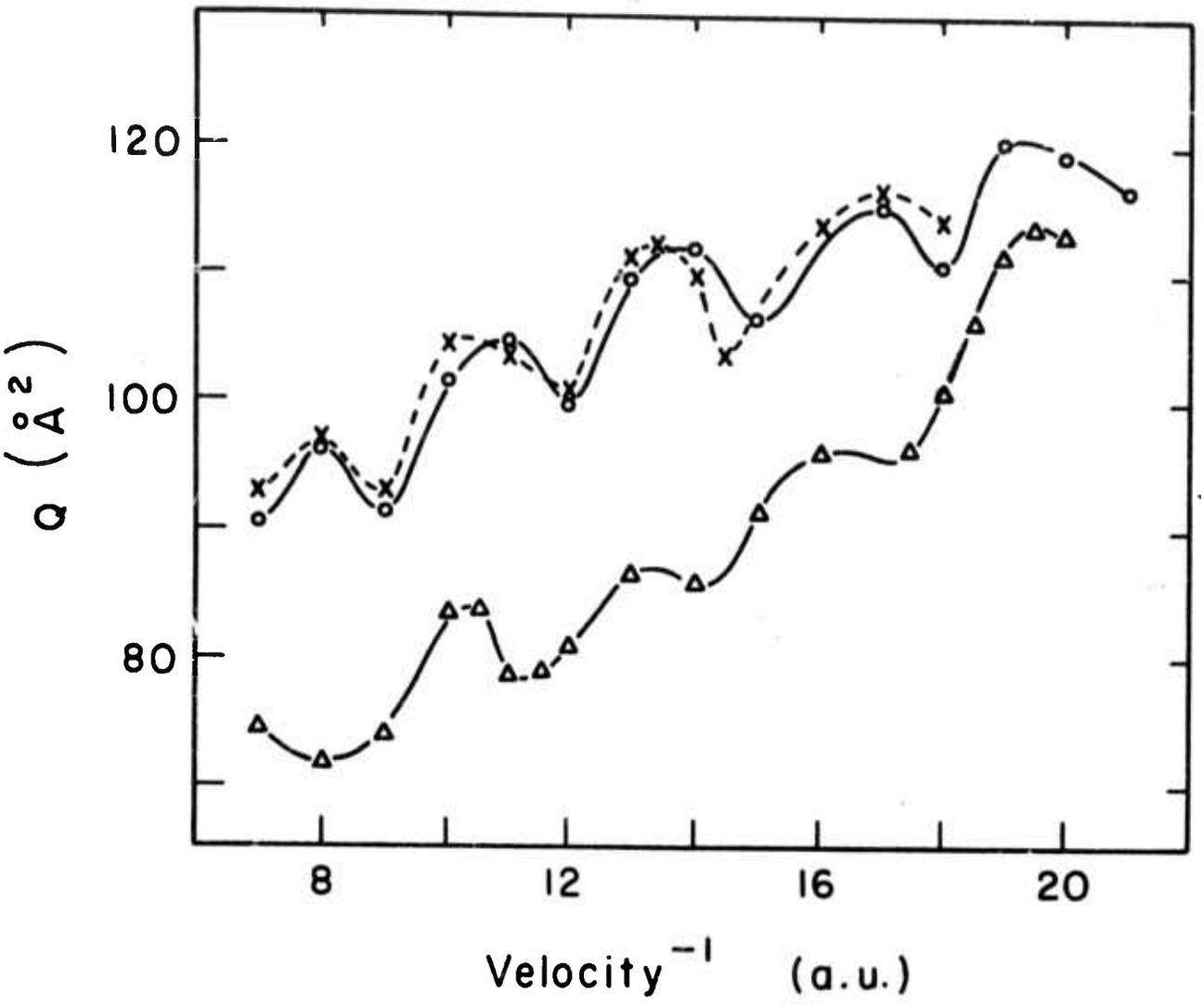

Fig. 1

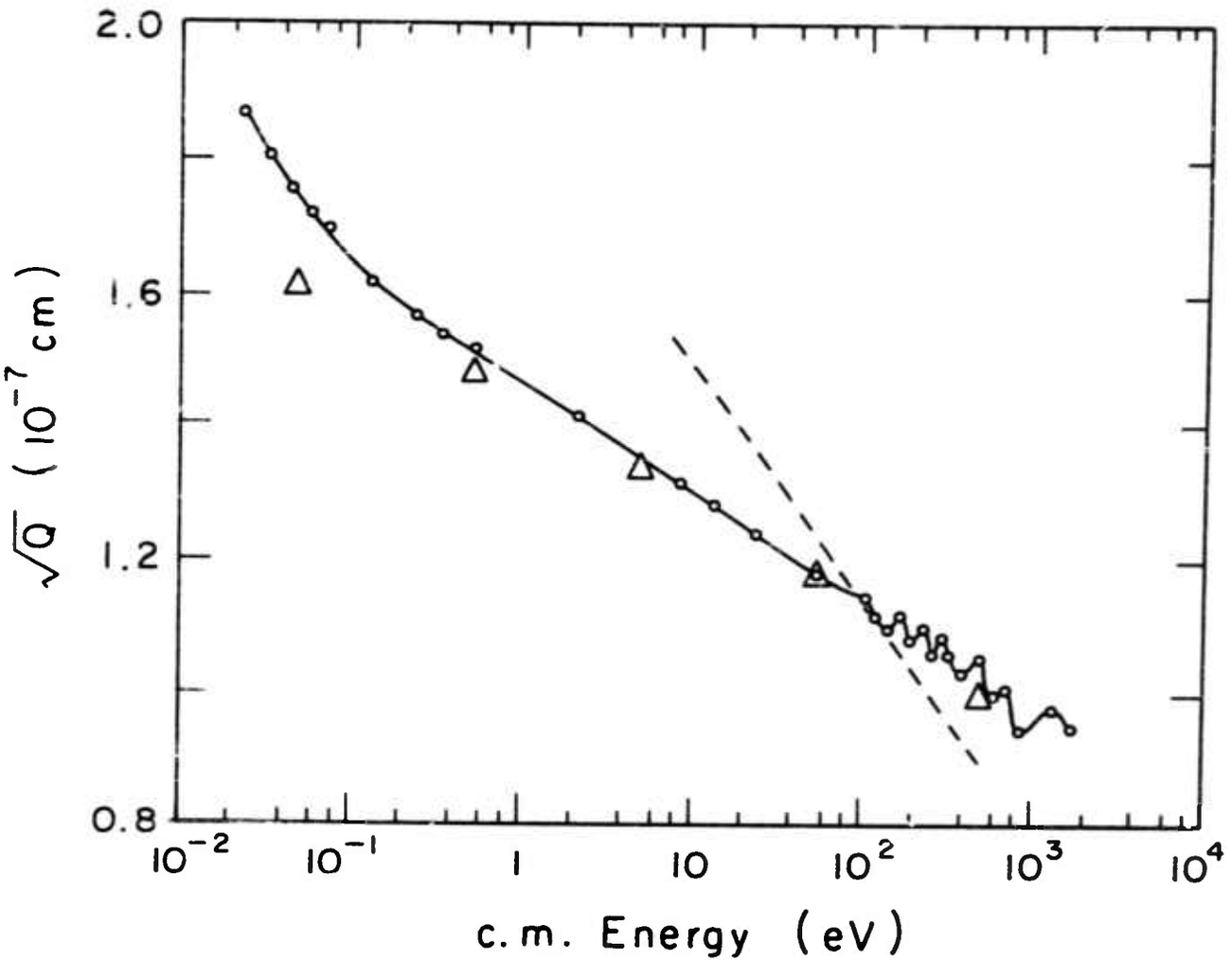

Fig. 2

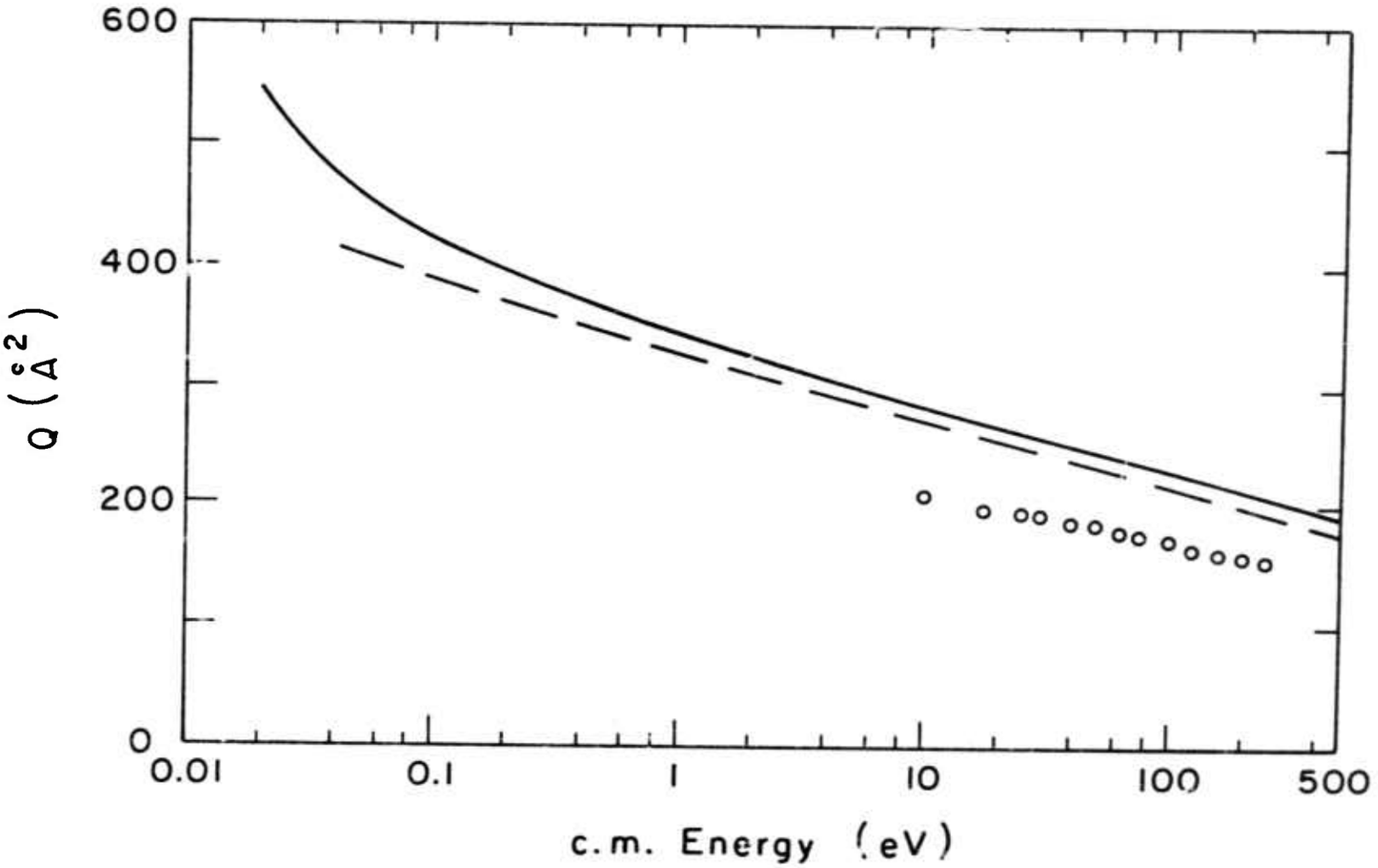

Fig. 3

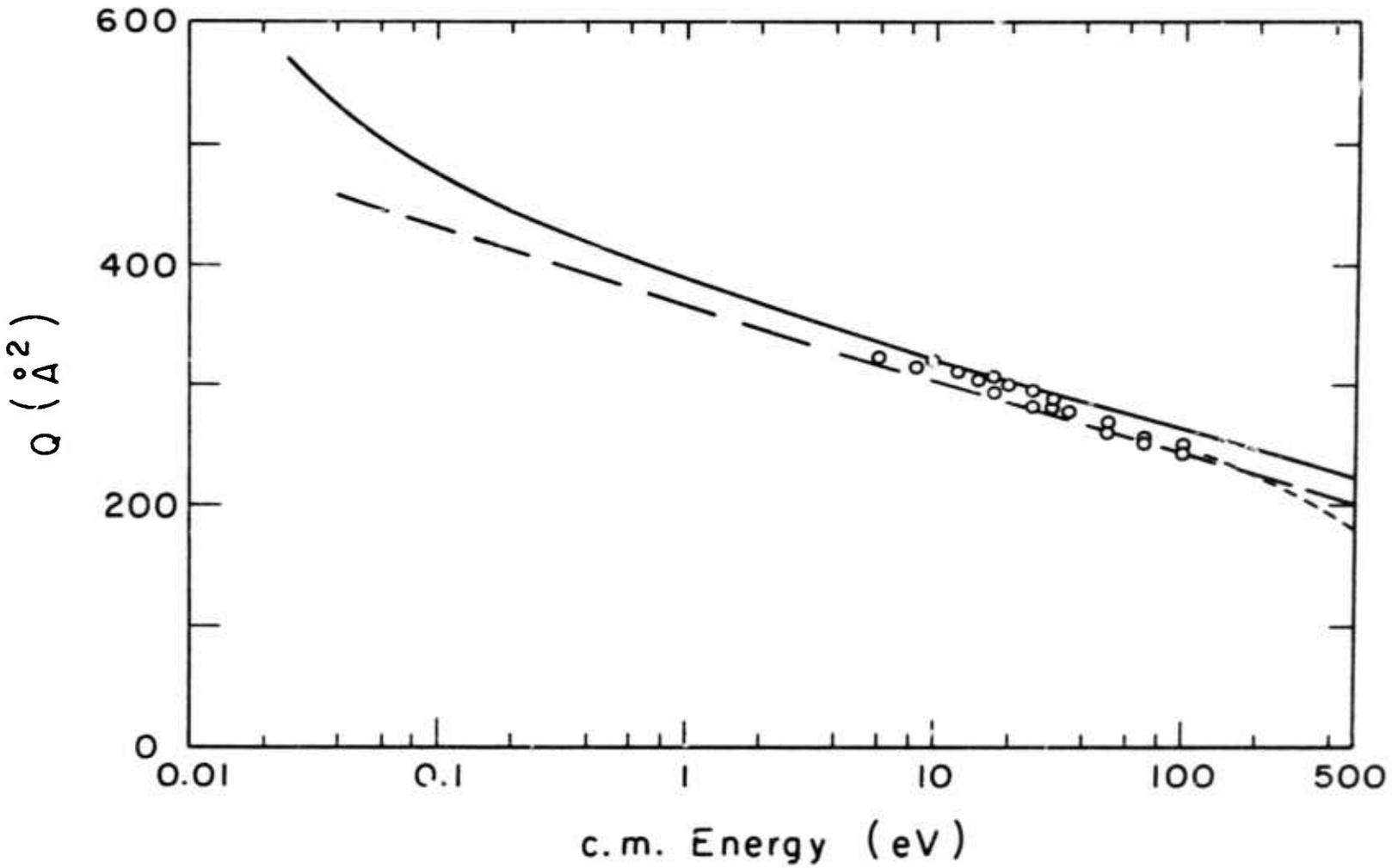

Fig. 4

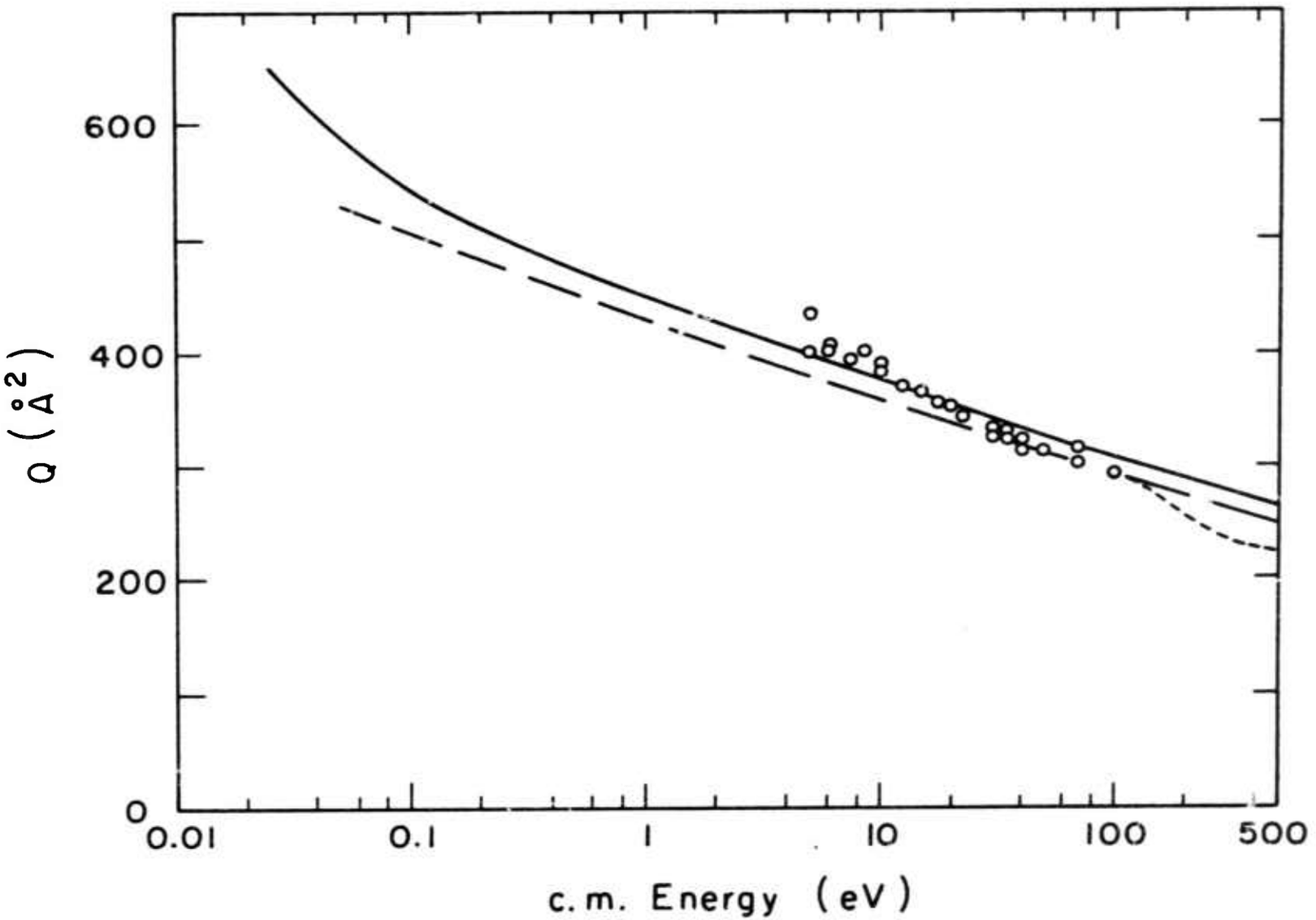

Fig. 5

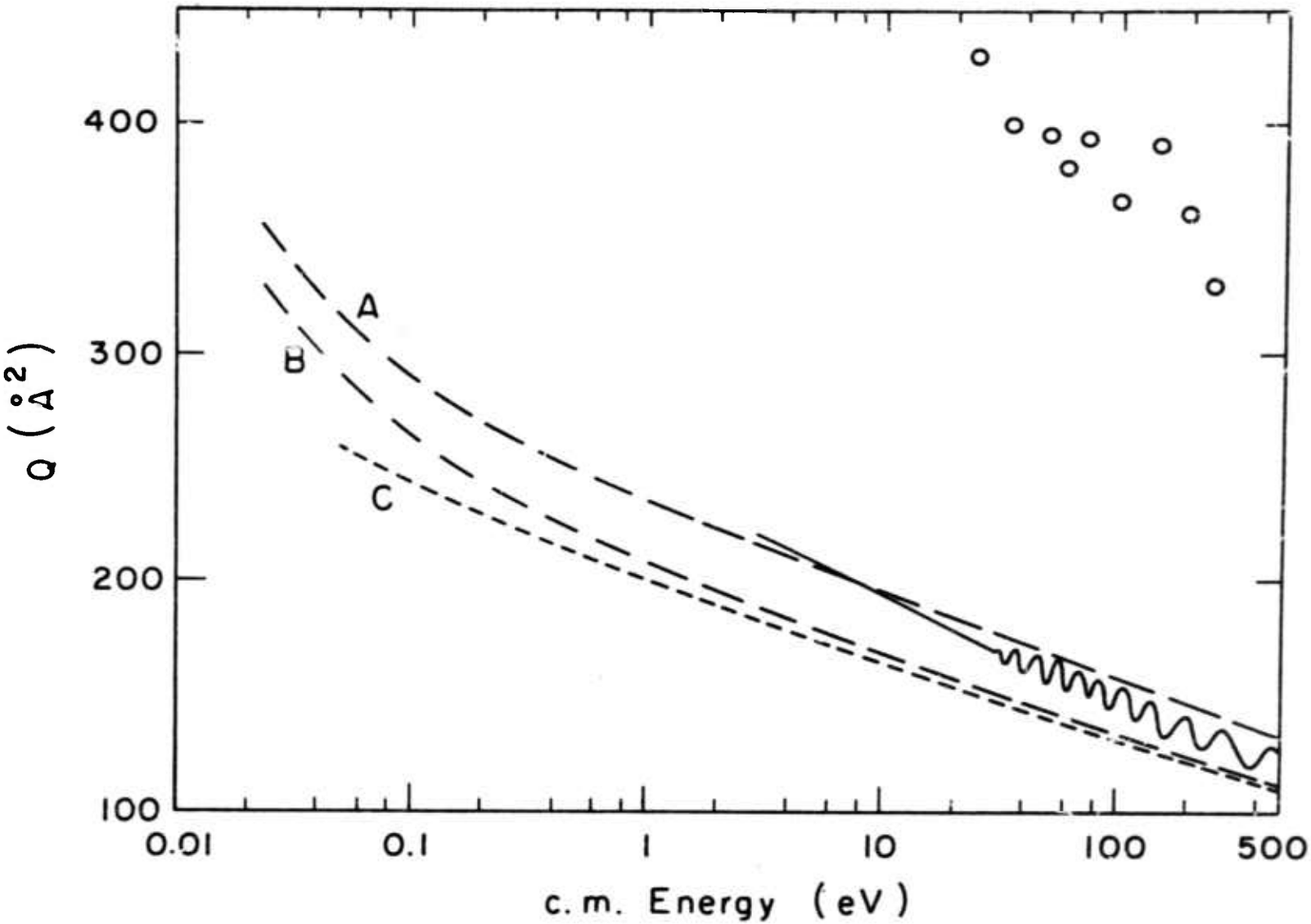

Fig. 6

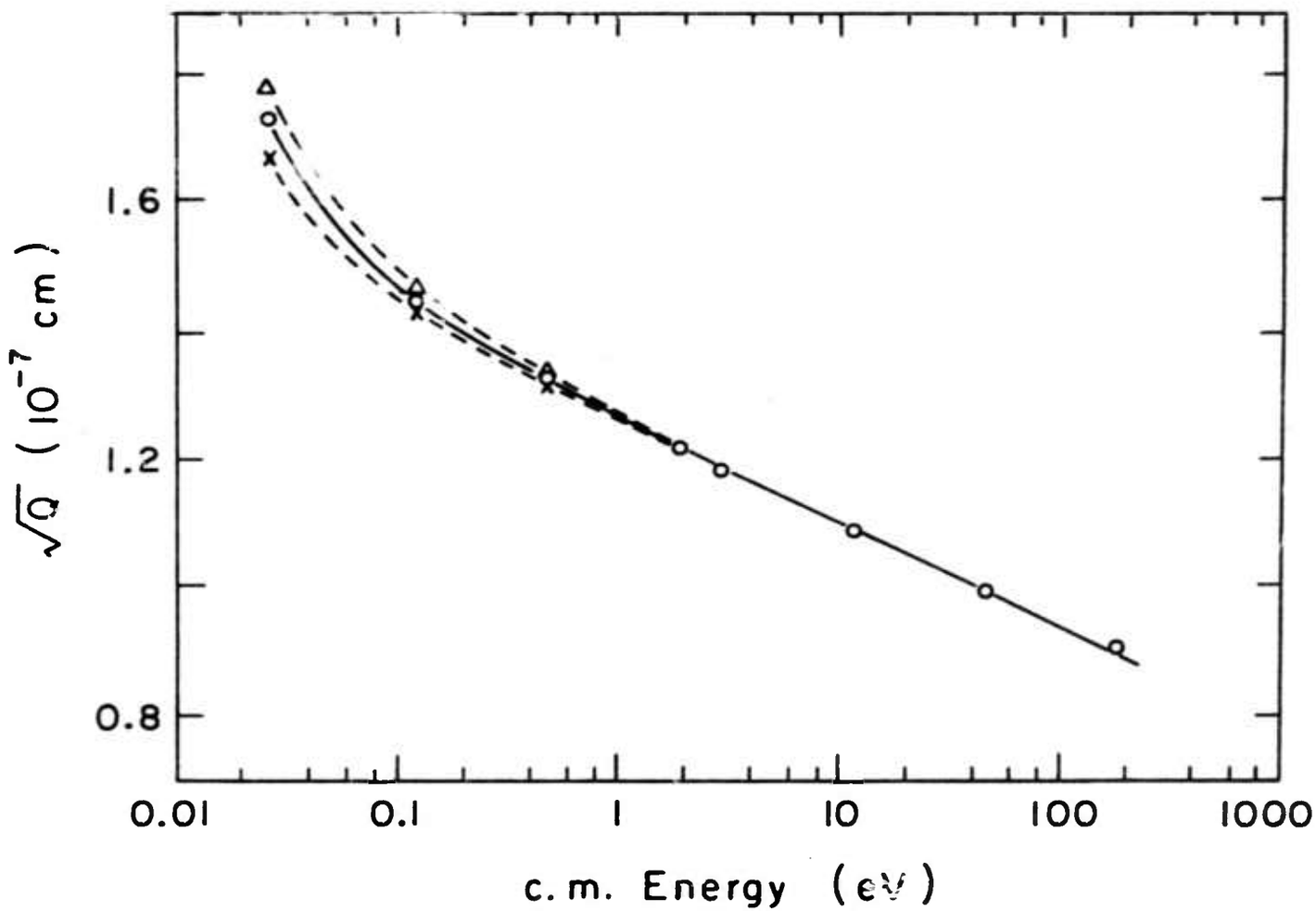

Fig. 7

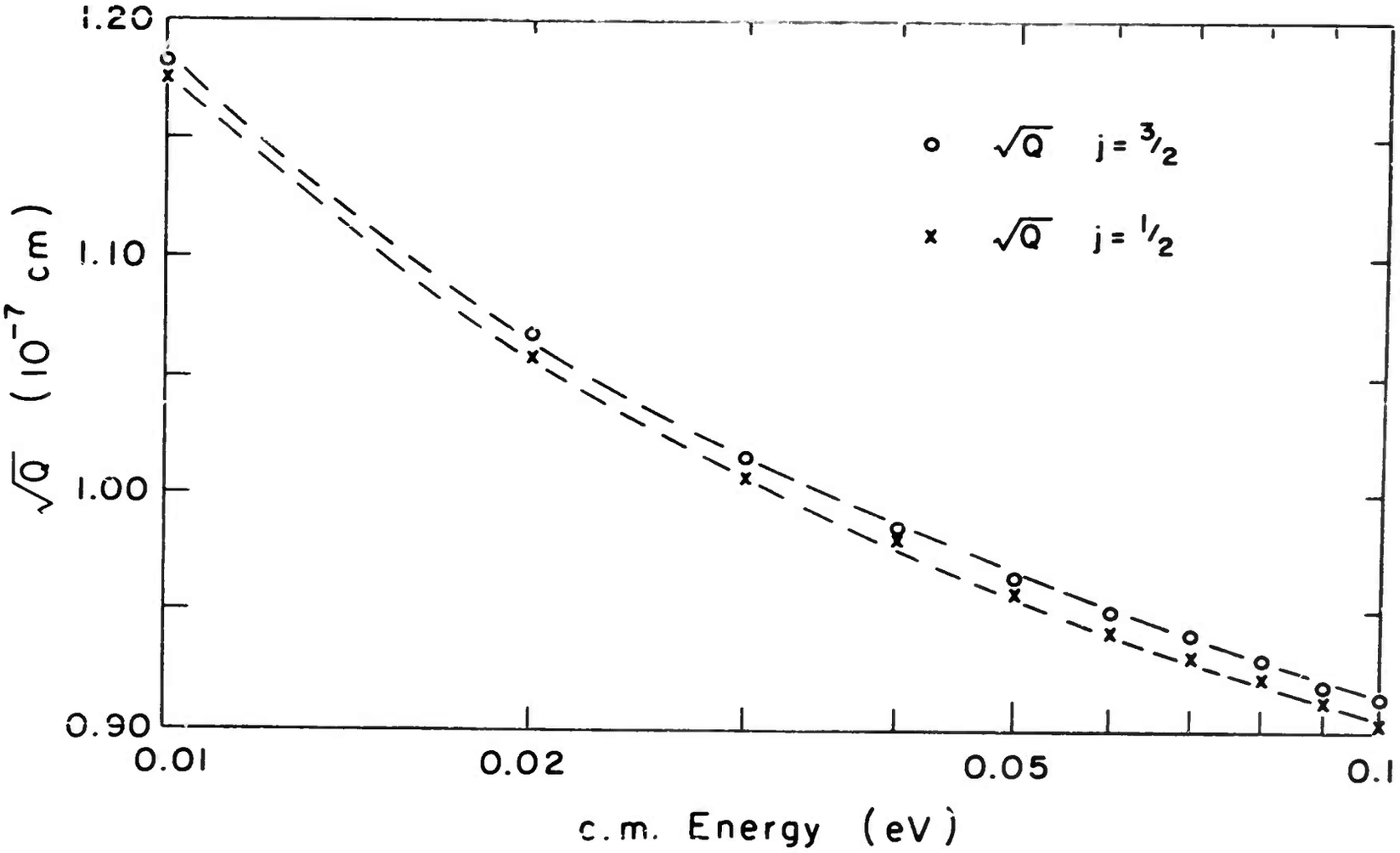
1.20
1.10
1.00
0.90
$\sqrt{Q}$ (10^{-7} cm)
0.01
0.02
0.05
0.1
c.m. Energy (eV)
o $\sqrt{Q}$ j = 3/2
x $\sqrt{Q}$ j = 1/2

Fig. 8

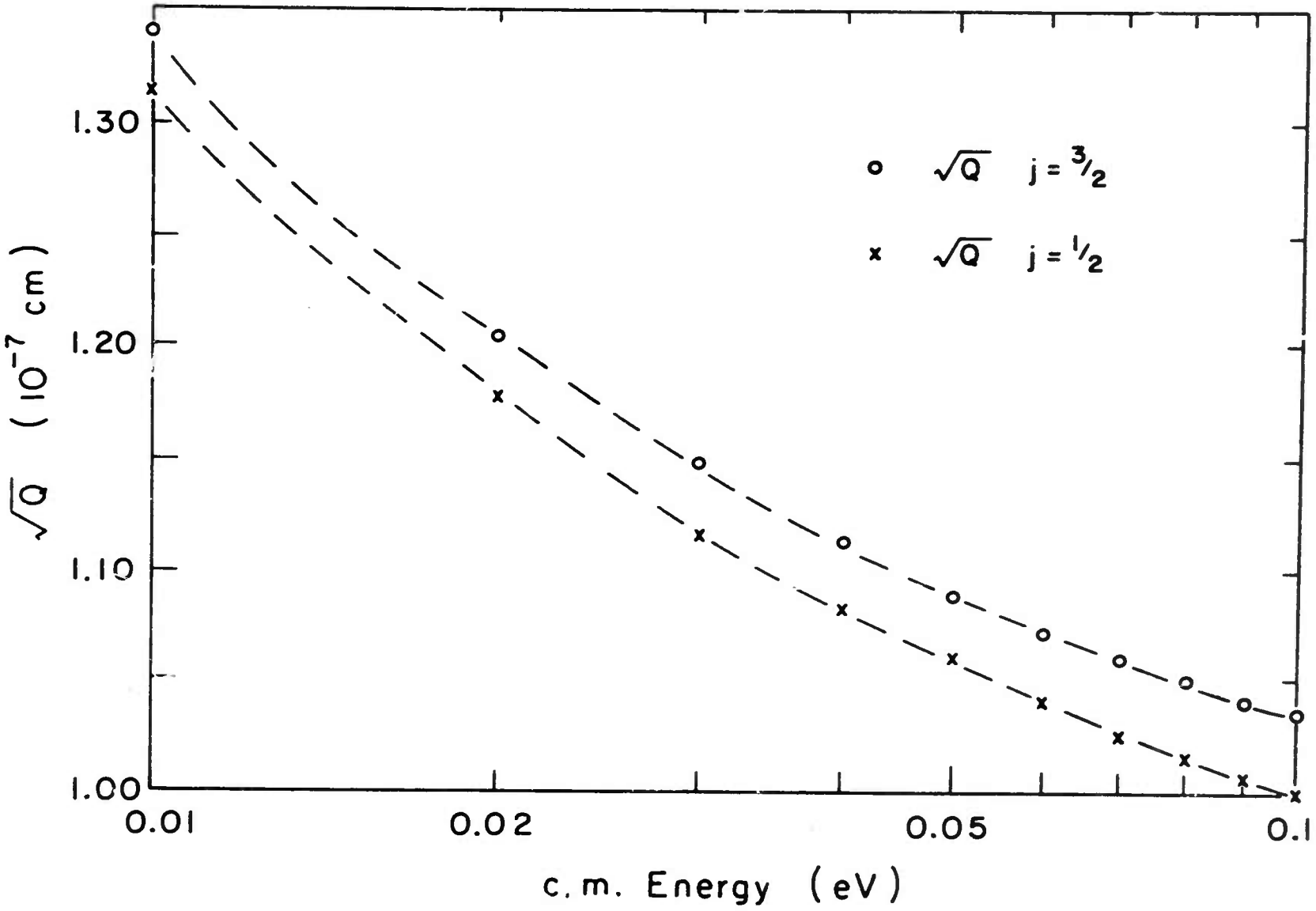
1.30
1.20
1.10
1.00
$\sqrt{Q}$ (10^{-7} cm)
0.01
0.02
0.05
0.1
c.m. Energy (eV)
o $\sqrt{Q}$ j = 3/2
x $\sqrt{Q}$ j = 1/2

Fig. 9